

7.5 Calibration Gases

7.5.1 Permeation tubes, one each of H₂S, MeSH, DMS, and DMDS, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7.5.2 Cylinder Gases. Cylinder gases may be used as alternatives to permeation devices. The gases must be traceable to a primary standard (such as permeation tubes) and not used beyond the certification expiration date.

7.6 Citrate Buffer and Sample Line Loss Gas. Same as Method 15, Sections 7.6 and 7.7.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 15, Section 8.0, except that the references to the dilution system may not be applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample line loss check	Ensures that uncorrected negative bias introduced by sample loss is no greater than 20 percent, and provides for correction of bias of 20 percent or less.
8.0	Calibration drift test	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 5 percent.
10.0	Analytical calibration	Ensures precision of analytical results within 5 percent.

10.0 Calibration and Standardization

Same as Method 15, Section 10.0, with the following addition and exceptions:

10.1 Use the four compounds that comprise TRS instead of the three reduced sulfur compounds measured by Method 15.

10.2 Flow Meter. Calibration before each test run is recommended, but not required; calibration following each test series is mandatory. Calibrate each flow meter after each complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by 5 percent or more, the completed test runs must be voided. Alternatively, the flow data that yield the lower flow measurement may be used. Flow over the permeation device may also be determined using a soap bubble flowmeter.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see Section 8.0).

12.0 Data Analysis and Calculations

12.1 Concentration of Reduced Sulfur Compounds. Calculate the average concentration of each of the four analytes (*i.e.*, DMDS, DMS, H₂S, and MeSH) over the sample run (specified in Section 8.2 of Method 15 as 16 injections).

$$C = \frac{\sum_{i=1}^N S_i}{N} \quad \text{Eq. 16-1}$$

Where:

S_i = Concentration of any reduced sulfur compound from the *i*th sample injection, ppm.

C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.

N = Number of injections in any run period.

12.2 TRS Concentration. Using Equation 16-2, calculate the TRS concentration for each sample run.

$$C_{\text{TRS}} = d \sum (C_{\text{H}_2\text{S}} + C_{\text{MeSH}} + C_{\text{DMS}} + 2C_{\text{DMDS}}) \quad \text{Eq. 16-2}$$

Where:

C_{TRS} = TRS concentration, ppmv.

C_{H₂S} = Hydrogen sulfide concentration, ppmv.

C_{MeSH} = Methyl mercaptan concentration, ppmv.

C_{DMS} = Dimethyl sulfide concentration, ppmv.

C_{DMDS} = Dimethyl disulfide concentration, ppmv.

d = Dilution factor, dimensionless.

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12.3 Average TRS Concentration. Calculate the average TRS concentration for all sample runs performed.

$$\text{Average TRS} = \frac{\sum_{i=1}^n \text{TRS}_i}{N(1 - B_{wo})} \quad \text{Eq. 16-3}$$

Where:

Average TRS = Average total reduced sulfur in ppm.

TRS_i = Total reduced sulfur in ppm as determined by Equation 16-2.

N = Number of samples.

B_{wo} = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases.

13.0 Method Performance

13.1 Analytical Range. The analytical range will vary with the sample loop size. Typically, the analytical range may extend from 0.1 to 100 ppmv using 10- to 0.1-ml sample loop sizes. This eliminates the need for sample dilution in most cases.

13.2 Sensitivity. Using the 10-ml sample size, the minimum detectable concentration is approximately 50 ppb.

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14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. O'Keeffe, A.E., and G.C. Ortman. "Primary Standards for Trace Gas Analysis." *Analytical Chemical Journal*, 38,76. 1966.
2. Stevens, R.K., A.E. O'Keeffe, and G.C. Ortman. "Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per-Million Levels." *Environmental Science and Technology*, 3:7. July 1969.
3. Mulik, J.D., R.K. Stevens, and R. Baumgardner. "An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities." Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA. April 6-8, 1971.
4. Devonald, R.H., R.S. Serenius, and A.D. McIntyre. "Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds." *Pulp and Paper Magazine of Canada*, 73,3. March 1972.
5. Grimley, K.W., W.S. Smith, and R.M. Martin. "The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van." Presented at the 63rd Annual APCA Meeting, St. Louis, MO. June 14-19, 1970.
6. General Reference. *Standard Methods of Chemical Analysis*, Volumes III-A and III-B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.

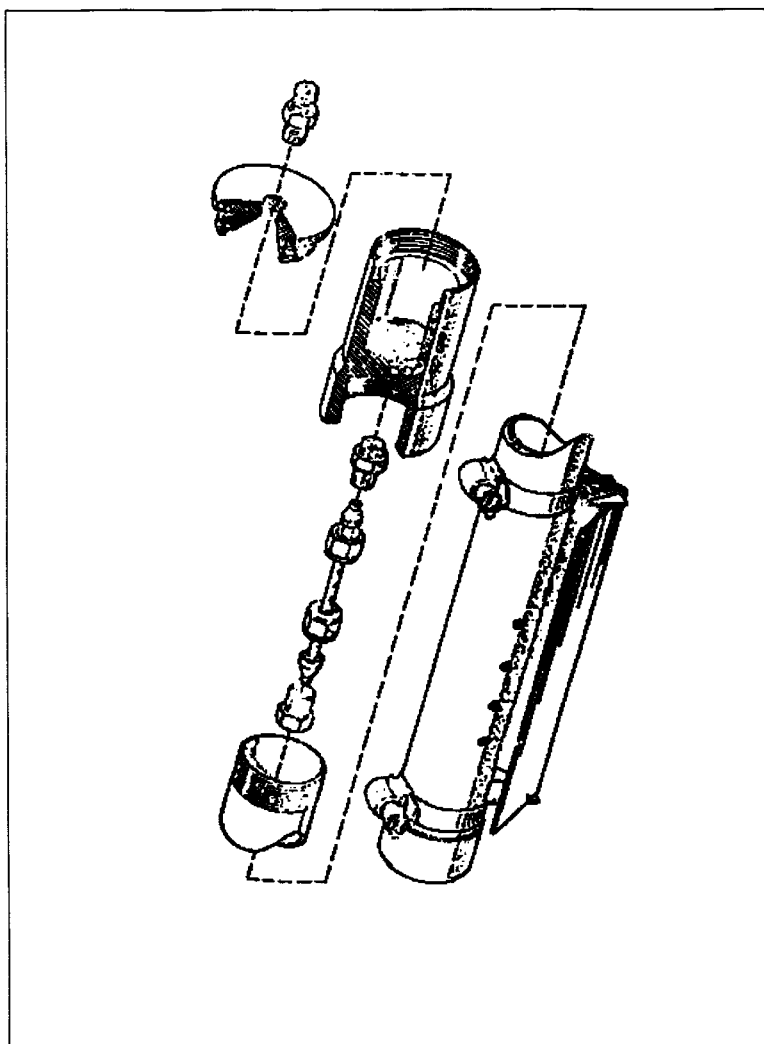


Figure 16-1. Probe used for Sample Gas Containing High Particulate Matter Loading.

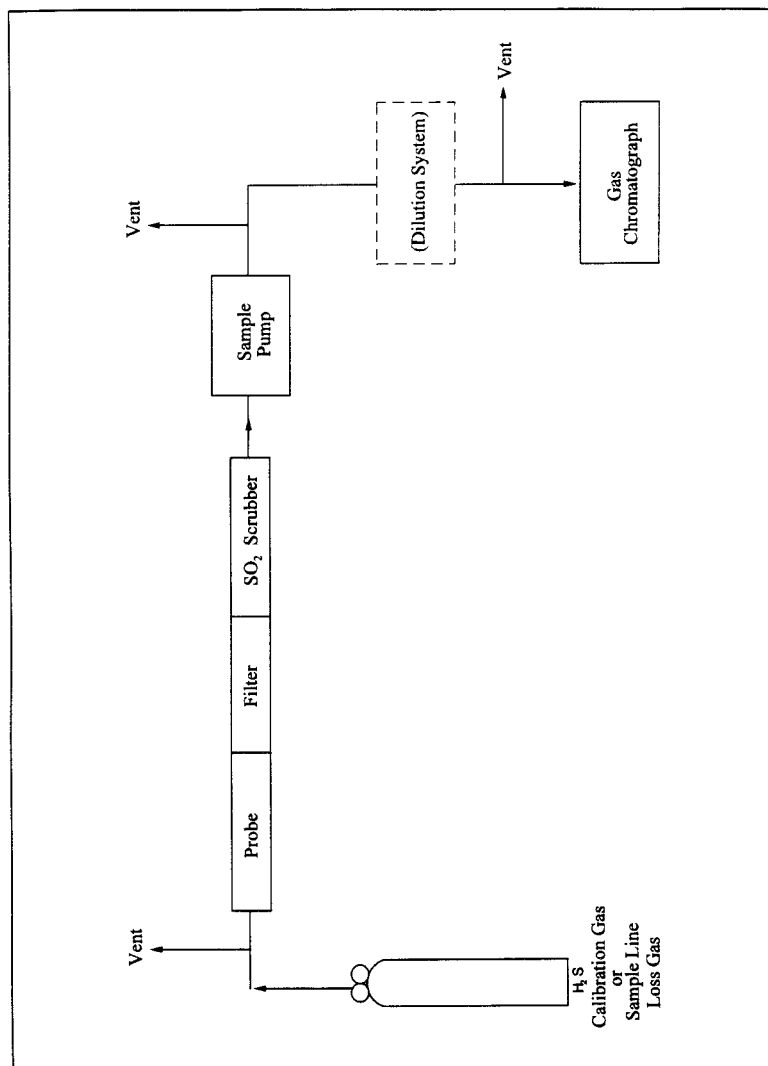


Figure 16-2. Calibration System.

METHOD 16A—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES (IMPINGER TECHNIQUE)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6, and Method 16.

1.0 Scope and Application

1.1 Analytes.